Copy 756820 -1

THEORETICAL ASPECTS OF ELECTRON CORRELATIONS IN ELECTRON COLLISIONS

By

Mitio Inokuti

Prepared For Presentation at the
NATO Advanced Study Institute
on Photoionization and Other Probes
of Many-Electron Interactions
August 31 to September 13, 1975
Carry-le-Rouet, France

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

U of C-AUA-USERDA

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

**operated under contract W-31-109-Eng-38 for the
U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED &B

THEORETICAL ASPECTS OF ELECTRON CORRELATIONS IN ELECTRON COLLISIONS*

Mitio Inokuti

Argonne National Laboratory

9700 S. Cass Avenue, Argonne, Illinois 60439, U.S.A.

ABSTRACT

Electron-correlation effects manifest themselves in diverse facets of electron collision with an atom or molecule. A fast incident electron acts largely as an external agent, and its inelastic collisions probe the structure, including correlations within the target (in both the initial state and the final state), nearly in the same way as photoionization processes do. In inelastic collisions of a slow electron, the central object of study is the correlated motion of the incident electron and an electron excited out of the target core. This elementary observation is illustrated in the lecture by many examples and is elaborated by remarks on some current theoretical methods.

1. INTRODUCTION

1.1. Electrons Versus Photons. How are They Different?

Electron collisions are much richer than photoionization in the variety of phenomena and data. On one hand, the variety of phenomena shows up as soon as one examines electron collisions at different kinetic energies. On the other hand, the variety of data

* Work performed under the auspices of the U.S. Energy Research and Development Administration.

is exemplified by terms such as "total," "differential," and "multiply differential," which indicate alternative levels of detail with which one looks at electron collisions. In compensation, the electron-collision data are usually of lower resolution.

The fundamental difference of electron collision from photo-absorption is the nonspecificity of excitation; an electron usually delivers to an atom or molecule only a fraction of its kinetic energy, while a photon (in the energy range of our interest) becomes completely absorbed in a single event. In other words, an energy delivered by each electron collision must be determined through observation (either of the scattered electron or of the target state after the collision).

1.2. Fast Electrons and Slow Electrons

It is useful to classify electron collisions into two kinds. The criterion of the classification is whether an incident electron is fast or slow compared to the internal motion of atomic electrons that pertain to a phenomenon under consideration. Electrons of a few-keV energy, for example, are fast with respect to all discrete excitations and to the majority of ionizing collisions with He, but are not fast with respect to the K-shell ionization of Ar. Phrased in sharper terms, the crucial distinction is whether the incident electron stays in the course of interactions as an external agent separate from the atomic electrons or it becomes incorporated into the target at least for a period of time. (Elastic collisions of electrons have less bearing on electron correlations, and therefore are outside the main theme of the present discussion.)

2. FAST ELECTRONS

2.1. Elements of the Bethe Theory

Following Bethe [1,2], we treat the action of a fast electron as a weak perturbation, i.e., within the first Born approximation. Numerous results thus obtained are powerful as a framework of general understanding, as fully discussed in Refs. 3-5.

Bethe's initial point is that the momentum transfer $\hbar\vec{K}$ from the electron to an atom or molecule is a key variable. Suppose that an electron of kinetic energy T (assumed nonrelativistic, i.e., $T < 10$ keV) excites an atomic state n at excitation energy E_n measured from the ground state 0. The differential cross section is

given as

$$d\sigma_n = \frac{4\pi a_0^2}{T/R} \cdot \frac{f_n(K)}{E_n/R} \cdot d[\ln(Ka_0)^2], \quad (1)$$

where $a_0 = 0.529 \times 10^{-8}$ cm is the Bohr unit of length and $R = 13.6$ eV is the Rydberg unit of energy. The quantity $f_n(K)$ is the generalized oscillator strength (GOS) defined by

$$f_n(K) = (E_n/R)(Ka_0)^{-2} \left| \langle n | \sum_j \exp(i\vec{K} \cdot \vec{r}_j) | 0 \rangle \right|^2, \quad (2)$$

where $\vec{r}_j$ is the position of the j th atomic electron and $\langle n | \quad | 0 \rangle$ represents a matrix element between atomic states n and 0 .

When the atomic final state belongs to a continuum, it is appropriate to consider the doubly differential cross section $(d/dE)(d\sigma)$ in place of $d\sigma_n$, the excitation energy E now being a continuous variable. Also, one defines the GOS density $df(K,E)/dE$ per unit range of E through replacing the index n by d/dE in Eqs. (1) and (2). Sometimes it is necessary to consider a finer breakdown of the cross section and the GOS, specified, e.g., by the energy and direction of an ejected electron resulting from fixed E .

Thus, the analysis of fast collisions reduces to the study of an atomic matrix element, just as the analysis of the photoeffect does. The similarity to the photoeffect is not only formal but deep-rooted in the physics. When the incident electrons is scattered by a small angle, the momentum transfer $\hbar K$ is small. Intuitively, such a collision may be characterized by a large impact parameter* b . The force then exerted by the incident electron is uniform over the spatial extent of the atom, in the same way as implied by the dipole approximation for photoabsorption. Yet the same force is sharply peaked in time owing to the high velocity of the incident electron, and therefore its Fourier components are widely distributed in frequency ω . Each of the Fourier components excites the atomic state at $E = \hbar\omega$. Consequently, electron collisions at small K are similar to irradiation with a photon flux having a wide and calculable spectrum.

* The variables K and b are roughly complementary to each other in the sense of Fourier analysis so that most collisions satisfy the relation $Kb \approx 1$.

To see this connection mathematically, one may expand the exponential in Eq. (2) and write the small-K behavior of $f_n(K)$ as

$$f_n(K) = f_n + (Ka_0)^2 f_n^{(1)} + \frac{1}{2} (Ka_0)^4 f_n^{(2)} + \dots, \quad (3)$$

where

$$f_n = (E_n/R) \left| \langle n | \sum_j x_j | 0 \rangle \right|^2 \quad [x_j = (\vec{K} \cdot \vec{r}_j)/K] \quad (4)$$

is the dipole oscillator strength for the transition $0 \rightarrow n$, and $f_n^{(1)}$ and $f_n^{(2)}$ are combinations of certain matrix elements (p. 312 of Ref. 3). Thus, in principle, we expect to see in electron collisions at small K whatever correlation effects we see in photo-absorption.

There are some differences between electron collisions and photoabsorption, however. First of all, the limit $K \rightarrow 0$ is never precisely realized in electron collisions. The smallest K value for fixed E and T occurs at zero scattering angle, and is given by

$$(K_{\min} a_0)^2 \cong E^2/(4RT) \quad (5)$$

where $E/T \ll 1$. The value of $(K_{\min} a_0)^2$ is decisive for consideration of the non-dipole contributions expressed by the second and higher terms in Eq. (3). Second, by studying the K-dependence of $f_n(K)$, one can learn much about non-dipole excitations, which are often quite sensitive to electron correlations. For example, the $f^{(1)}$ value for the $1^1S \rightarrow 2^1S$ excitation of He is 0.13 according to a Hartree-Fock calculation, and is 0.084 according to a calculation including correlation effects [6].

Large-angle scattering is characterized by large K, i.e., by small b. If $\hbar K$ greatly exceeds the average momentum of atomic electrons, the role of electron binding should be inappreciable and the cross section should approximate the Rutherford cross section multiplied by Z, the number of atomic electrons. In other words, we should get $Z/(Ka_0)^2$ in place of $(R/E_n)f_n(K)$ in Eq. (1) and the GOS is nonvanishing only when $E \cong (\hbar K)^2/2m$. Equation (2) endorses this expectation. For large K, $\exp(i\vec{K} \cdot \vec{r}_j)$ is strongly oscillatory in the configuration space. The matrix element therefore must vanish unless the product of the wavefunctions for initial and final states behave nearly as $\exp(-i\vec{K} \cdot \vec{r})$, i.e., unless one of the atomic electrons receives the entire momentum transfer $\hbar K$.

To put this argument more precisely, one can show that (p. 336 of Ref. 3)

$$\frac{df(K, E)}{dE} \cong \frac{E/R}{(Ka_0)^2} \sum_j \left\langle \delta \left(\frac{(\hbar K)^2}{2m} + \frac{\hbar \vec{K} \cdot \vec{p}_j}{m} - E \right) \right\rangle, \quad (6)$$

where $\vec{p}_j$ is the momentum of the j th atomic electron, $\langle \dots \rangle$ denotes the expectation value in the initial atomic state, and $(\hbar K)^2/2m$ is taken as much greater than the binding energy B of the atomic electrons. It is also possible to show that $df(K, E)/dE$ differs significantly from zero in the range

$$|(Ka_0)^2 - E/R| < \xi (E/B)^{\frac{1}{2}}, \quad (7)$$

where ξ is a constant of the order of magnitude of unity. We name the peaking of $df(K, E)/dE$ in the region (7) as the Bethe ridge and call this class of collisions quasi-free-electron scattering [7, 8], a subject of many recent measurements [9-12]. These measurements primarily probe the momentum distribution in the target, and are pertinent to electron correlations insofar as they influence the momentum distribution. Also, these measurements usually analyze ejected electrons in coincidence with the monitoring of scattered electrons, and therefore indicate a shell or subshell from which ejected electrons originate, giving a shellwise breakdown of $df(K, E)/dE$. Resulting data are often interpreted in a way similar to photoelectron data by use of the notions such as electron shake-off, even though the mechanism of excitation greatly differs from photoeffect.

An important result concerns the T -dependence of the excitation cross section σ_n , i.e., the integral of Eq. (1) over all possible K . One can show in general that

$$\sigma_n = 4\pi a_0^2 (R/T) [(f_n R/E_n) \ln(4c_n T/R) + O(E_n/T)], \quad (8)$$

where c_n is a constant derived from $f_n(K)$ (p. 325 of Ref. 3). As first pointed out by Fano [13], a plot of $T\sigma_n$ versus $\ln T$ should behave as a straight line for $T \gg E_n$, and its slope is determined by f_n/E_n . The Fano plot enables one to extract f_n from electron-collision data.

For electrons with $T > 10^4$ eV, Eqs. (1) and (8) require modifications due to relativistic kinematics. (See p. 303 and p. 328 of Ref. 3.)

2.2. Electron Correlations and GOS

For He discrete excitations, extensive calculations [6, 14-18] show the importance of electron correlations in obtaining accurate GOS. Here, decisive effects come from correlations in the ground state, especially from angular correlations expressed by p^2 configurations [19].

As to discrete excitations in other atoms, recent calculations including correlation effects concern Mg, Ca, Sr, and Ba [20], Mg and Ca [21], Be and isoelectronic ions [22], Al [23], and Be, B, C, N, and O [24]. Although it is difficult to summarize the great volume of data, one can recognize a few points to be learned from these calculations. First, inclusion of correlations, especially angular correlations, normally allows the atom to contract and thus makes GOS significantly smaller than Hartree-Fock results at low K . The change of GOS at high K is often opposite. Second, all the calculations point to the importance of balanced treatment of the initial and final states; simultaneous improvement of the two states is necessary for good results. Third, sometimes introduction of electron correlations changes the character of GOS say from optically allowed to almost forbidden or vice versa. A most dramatic example [24] is the $2s^2 2p^3 \ 4S \rightarrow 2s 2p^4 \ 4P$ transition in N. Fourth, one sometimes sees marked influence of correlations upon GOS near its minima, either as a function of excitation energy or as a function of K (p. 319 of Ref. 3). The $3s^2 3p \rightarrow 3s^2 nd$ transitions in Al [23] exemplify this point. Finally, for heavy atoms such as Ba [20] or Hg and Au [25], both relativistic effects and correlation effects are important.

The GOS for transitions to continua is more difficult to evaluate, except in the neighborhood of the Bethe ridge. The bulk of the GOS at small and moderate K lies in low- E regions, for which final-state electron interactions with the remaining ion core are in general complicated. Provided the ground-state wavefunction is reasonably known, measurements of GOS may be considered as a probe of these interactions. Especially extensive data from coincidence measurements on scattered and ejected electrons [26, 27] should contain a great deal of physics, which so far theory has only scratched.

Examples of the continuum GOS calculations, including correlations, are not many. For He continua, calculations by Jacobs [28] and by Robb et al. [29, 30] appear to be most definitive. These calculations use accurate wavefunctions obtained by close-coupling

or R-matrix methods for the final state $e + \text{He}^+$, in which the outgoing electron is slow and therefore has ample time to be influenced by intricate interactions with the He^+ core, either in its ground state or in its excited state. Here we begin to see the intimate connection of fast-electron collisions with slow-electron collisions. Doubly excited states of He, degenerate with the single-ionization continuum, cause the well-known Beutler-Fano profile in the GOS, whose characteristics intricately depend upon K , and angle of ejection resulting from autoionization [28, 31, 32]. Double ionization of He results in final states in which two electrons are slowly moving out of the He^{++} ion. The GOS for the double ionization should contain a great deal of physics on two-electron correlations, which have been investigated only experimentally [33].

Amusia and co-workers [34 – 37] have studied effects of electron correlations on the continuum GOS of other rare gas atoms by use of the random-phase approximation with exchange. The correlation effects are most dramatically seen in the $3p \rightarrow \text{Ed}$ transition in Ar, in the optically forbidden transition $p \rightarrow \text{Ep}$, and in transitions of the inner s electrons into the Ep continuum.

3. SLOW ELECTRONS

3.1. Basic Observations

The dynamics of a slow-electron collision with an atom A is essentially concerned with excited states of the negative ion A^- , because the incoming slow electron becomes mechanically indistinguishable from outer atomic electrons during the collision. The dramatic manifestation of this observation is seen in resonances found for electron scattering by many atoms and molecules [38, 39]. The slow $e\text{-}A$ collision is therefore closely related to the final states [40–42] of the photoabsorption by A^- . Likewise, the slow $e\text{-}A^+$ collision is closely related to the photoabsorption of A , and the slow $e\text{-}A^{++}$ collision to the photoabsorption of A^+ . Notice that the correspondence of the electron collision with the photoabsorption involves the unit difference of the electron number in the initial target system.

Another principal distinction is that the final states in the photoabsorption are usually limited by dipole selection rules to a few angular momenta, whereas in the electron collision, there is only a loose limitation of angular momenta due to centrifugal forces. For example, the photoabsorption of H^- leads to ^1P final states, but

slow-electron collisions with H involve both singlet and triplet states with orbital characters S, P, D, etc., unless the electron energy is extremely small.

Moreover, the dynamics of slow inelastic collisions

is completely governed by correlations of two electrons that have energies much higher than the other electrons in the A^+ core. In this sense, electron correlations play an essential role in slow-electron inelastic collisions.

3.2. Electron Correlations in the Ground State

For illustration of several standard methods of treating electron correlations in general, let us consider briefly the ground state (1^1S) of two-electron systems such as He and H^- . As the starting point, let us consider the Hartree-Fock function

$$\psi = u(r_1)u(r_2) \quad (9)$$

where $\vec{r}_1$ and $\vec{r}_2$ are electron coordinates and $u(r)$ is an s orbital. (Throughout this section, spin variables are suppressed.) With the optimal $u(r)$, the function (9) gives 98.6% of the correct total energy for He, but gives many other properties unsatisfactorily.

The first kind of correlations, i.e., radial correlations, is described by the Eckart function

$$\psi = u(r_1)v(r_2) + v(r_1)u(r_2) \quad (10)$$

where $u(r)$ and $v(r)$ are different s orbitals. The importance of the radial correlations is easiest to see in H^- ; function (10) succeeds in giving the electron affinity reasonably, whereas function (9) fails in this respect. Yet the mean square radius $\langle (\vec{r}_1 + \vec{r}_2)^2 \rangle$ comes out too large (by 10% for He and by 50% for H^-).

The second kind of correlation is angular, and one way of expressing this is to write

$$\begin{aligned} \psi = & u(r_1)u(r_2) + \lambda [w_x(\vec{r}_1)w_x(\vec{r}_2) + w_y(\vec{r}_1)w_y(\vec{r}_2) \\ & + w_z(\vec{r}_1)w_z(\vec{r}_2)] \quad (11) \end{aligned}$$

where $w_x(\vec{r})$ is a p_x orbital and λ is a variational parameter. This function (11) exemplifies a general method of configuration interaction (CI), and may be denoted by abbreviations $s^2 + \lambda p^2$. Notice that the terms in the square brackets of Eq. (11) may be put in the form $(\vec{r}_1 \cdot \vec{r}_2) \times (\text{function of } r_1) \times (\text{function of } r_2)$, and therefore function (11) depends explicitly on the angle between $\vec{r}_1$ and $\vec{r}_2$. With this function we start obtaining nonvanishing values of $\langle \vec{r}_1 \cdot \vec{r}_2 \rangle$ and $\langle p_1 \cdot p_2 \rangle$. Further, one can generalize Eq. (11) into a form such as $s^2 + \lambda p^2 + \mu s' + \nu d^2 + \dots$, where $\lambda, \mu, \nu, \dots$ are parameters. Note that s' , i.e., a different s orbital, has been included; likewise, many different p and d orbitals may be included. (The above form shows configurations in the order of decreasing importance in He.)

Another way of generalizing Eq. (11) is to write

$$\psi = \sum_k \varphi_k(r_1, r_2) P_k(\cos \theta_{12}), \quad (12)$$

where P_k is the Legendre polynomial and $\cos \theta_{12} = (\vec{r}_1 \cdot \vec{r}_2)/r_1 r_2$. If we recall that

$$2r_1 r_2 \cos \theta_{12} = r_1^2 + r_2^2 - r_{12}^2, \quad (13)$$

where $r_{12} = |\vec{r}_1 - \vec{r}_2|$, we see that Eq. (12) is too restrictive; it contains only even powers of r_{12} , the crucial variable of the Coulomb potential $1/r_{12}$ between the electrons. Hylleraas' pioneering work demonstrates the merit of introducing odd powers of r_{12} and using a new set of variables $s = r_1 + r_2$, $t = r_1 - r_2$, $u = r_{12}$ in

$$\psi = e^{-\kappa s} \sum_{\alpha, \beta, \gamma} c(\alpha, \beta, \gamma) s^\alpha t^{2\beta} u^\gamma, \quad (14)$$

where κ and $c(\alpha, \beta, \gamma)$ are parameters, and α, β, γ are non-negative integers [43]. A further generalized form [44]

$$\psi = e^{-\kappa s} \sum_{\alpha, \beta, \gamma} c(\alpha, \beta, \gamma) s^{\alpha-\gamma} t^{2\beta} u^{\gamma-2\beta} \quad (15)$$

has been used also. The Hylleraas-type treatment has been exhaustively extended by Pekeris and co-workers [45-47].

Despite its great numerical success in variational calculations, the functional form (14) or (15) cannot be the exact solution [48]. Fock [49] showed that the exact solution has the form

$$\psi = e^{-\kappa s} \sum_{n=1,2,\dots} R^{2(n-1)} \sum_{p=0}^{[n-1]} g_{np}(\alpha, \theta_{12}) (\ln R)^p, \quad (16)$$

where

$$R = (r_1^2 + r_2^2)^{\frac{1}{2}} \quad (17)$$

and

$$\alpha = \tan^{-1}(r_2/r_1). \quad (18)$$

Fock's coordinates (R, α, θ_{12}) are a special case of the hyperspherical coordinates, which are appropriate for describing correlated motions in many-body systems in general. Indeed, these hyperspherical coordinates have been used in a general discussion of chemical reactions [50], in a formulation of atomic-structure calculations (Ref. 51 and references therein), and in other contexts to be taken up in the next section. Furthermore, numerical calculations specifically designed to simulate the Fock expansion, Eq. (16), have proved successful for the He ground state [47,52].

3.3. Theories of Slow-Electron Collisions

In this section I shall review some electron-collision theories from our special point of view, namely, the description of electron correlations. My discussion will be illustrative rather than exhaustive; it will concentrate on certain topics that I have chosen from numerous possibilities, and deliberately leave out some subjects that are taken up by other lecturers. Specifically, I shall omit discussion on numerical techniques.

Suppose that an electron of momentum $\hbar \vec{k}_0$ is incident on a neutral atom A in its ground state $\phi_0(\vec{r}_1, \dots, \vec{r}_N)$. After the collision one finds a scattered electron with momentum $\hbar \vec{k}_n$ and A in an eigenstate $\phi_n(\vec{r}_1, \dots, \vec{r}_N)$ at excitation energy E_n , where by energy conservation we have

$$(k_n a_0)^2 = (k_0 a_0)^2 - E_n/R. \quad (19)$$

The problem is to find the wavefunction of the A^- system under the boundary condition

$$\begin{aligned} \psi(\vec{r}_1, \dots, \vec{r}_N, \vec{r}_{N+1}) &\rightarrow \phi_0(\vec{r}_1, \dots, \vec{r}_N) \exp(i \vec{k}_0 \cdot \vec{r}_{N+1}) \\ &+ \sum_n \phi_n(\vec{r}_1, \dots, \vec{r}_N) A_n(\hat{k}_n) r_{N+1}^{-1} \exp(i \vec{k}_n \cdot \vec{r}_{N+1}), \end{aligned} \quad (20)$$

as the scattered-electron position $\vec{r}_{N+1}$ tends to infinity. (For brevity, spin variables are suppressed.) The function $A_n(\hat{k}_n)$ is to be determined by calculation, and is called the scattering amplitude, from which all cross sections may be evaluated. The summation runs over all n for which $(k_n a_0)^2 > 0$. (Formalistically speaking, the summation includes continua to allow for ionization, but a precise form of the boundary condition for ionization is a complicated issue.) For collisions with an ion, say A^+ , Eq. (20) must be modified to account for the asymptotic Coulomb force. This modification is tedious to describe, but is straightforward. This completes the statement of the problem.

By far the best known method of solution is the close-coupling method [53-56]. For the $e + A$ collision, one writes the wavefunction as

$$\psi(\vec{r}_1, \dots, \vec{r}_{N+1}) = \Omega \sum_{n=0}^{\infty} \phi_n(\vec{r}_1, \dots, \vec{r}_N) F_n(\vec{r}_{N+1}), \quad (21)$$

where Ω is an appropriate antisymmetrization operator, and $F_n(\vec{r})$ is a continuum orbital. Each term with fixed n represents a channel and the label n is called the channel index. The summation includes open channels ($k_n^2 > 0$) as well as closed channels ($k_n^2 < 0$). By treating Eq. (21) as a trial function in the Kohn variational principle, one obtains a set of simultaneous integro-differential equations for $F_n(\vec{r})$, similar in form to Hartree-Fock equations. Equivalently, one may take projections of the Schrödinger equation of the A^- system

$$(H - E)\psi = 0 \quad (22)$$

onto ϕ_n to arrive at the same result.

A basic argument for expansion (21) is that the totality of ϕ_n forms a complete set of functions and therefore any ψ should be expressible as Eq. (21), provided sufficiently many channels are included. This argument is indeed correct, and apparently is substantiated by considerable success of the method in many examples (as seen in Refs. 54-56). But it is unrealistic to say that one could always include as many channels as one wishes to obtain a good description of ψ . To appreciate this observation, we just have to recall the general structure of atomic energy levels. For any neutral atom, the energy levels become more and more dense as the first ionization energy I is approached, and then form continua above I , as forcefully discussed in Ref. 57.

The effect of the channel truncation is often discussed by use of Feshbach projection operators [58]. If P projects any operand onto included channels ($0 \leq n \leq n_t$) and Q onto excluded channels ($n_t < n$), the Schrödinger equation (22) may be rewritten as

$$P(H - E)(P + Q)\psi = 0, \quad (23)$$

$$Q(H - E)(P + Q)\psi = 0. \quad (24)$$

Solving Eq. (24) for $Q\psi$ as

$$Q\psi = -Q[Q(H - E)Q]^{-1}QHP\psi \quad (25)$$

and putting this into Eq. (23), we obtain

$$P\{H - PHQ[Q(H - E)Q]^{-1}QHP - E\}P\psi = 0. \quad (26)$$

The truncated close-coupling equation

$$P(H - E)P\psi = 0 \quad (27)$$

differs from the exact equation (26) in not having the so-called optical potential

$$V_{\text{opt}} = -PHQ[Q(H - E)Q]^{-1}QHP. \quad (28)$$

It can be shown that at energies below the lowest excitation threshold not included in the expansion, V_{opt} is real and negative; in other words, Eq. (27) contains a fictitious repulsive potential owing to the truncation. At higher energies, V_{opt} becomes complex to account for loss of electron flux to excluded channels.

One way of diminishing the truncation effect is to use in Eq. (21) a set of suitably chosen functions χ_n instead of atomic eigenfunctions ϕ_n . The functions χ_n , called pseudo-states, are in general superpositions of ϕ_n including highly excited states and continuum states, chosen, for example, to give the long-range asymptotic behavior of V_{opt} [59, 60]. There is no general principle for the choice of the pseudo-states, apart from numerical efficiency.

Let us look at Eq. (21) again and compare its structure with various ground-state wavefunctions discussed in Sec. 3.2. Equation (21) treats the incident electron quite differently from the atomic electrons; $F_n(\vec{r}_{N+1})$ are determined numerically by solving the close-coupling equations over the entire spatial region, while $\phi_n(\vec{r}_n, \dots, \vec{r}_N)$ are simply presumed known in advance and are non-vanishing in a limited spatial domain. This sharp distinction between the incident electron and the atomic electrons originates from the boundary condition, Eq. (20), and Eq. (21), indeed, is a reasonable approxima-

tion for very low energies and for large r_{N+1} , i.e., in the beginning and toward the end of the collision process. But when the incident electron is close to the middle of the atom, its motion should be highly correlated with the atomic electrons, especially with the one that becomes excited. This situation is formally similar to the ground-state correlation, which one may describe, e.g., by simultaneously optimizing the two orbitals $u(r)$ and $v(r)$ in Eq. (10); an optimization of say $u(r)$ under fixed $v(r)$ would lead to a poor result.

Equation (21) specializes into

$$\psi(\vec{r}_1, \vec{r}_2) = \sum_n [\phi_n(\vec{r}_1) F_n(\vec{r}_2) \pm \phi_n(\vec{r}_2) F_n(\vec{r}_1)] \quad (29)$$

for two-electron systems such as $e - H$ or $e - He^+$, where the plus sign applies to a singlet state and the minus sign to a triplet state. We may add to Eq. (29) Hylleraas-type terms [Eq. (14) for the total S state], then the trial function becomes capable of describing short-range correlations [61]. Alternatively, we may add to Eq. (29) CI-type terms [Eq. (11) for the total S state], which decay at large distances as bound-state orbitals [62-64]. An extreme idea in this direction is to abandon the close-coupling expansion altogether and to supplement Eq. (14) merely by terms necessary to satisfy the boundary condition for scattering. Thus, Schwartz [65] succeeded in obtaining the most accurate result for 1S and 3S $e - H$ states, although the calculation is limited to energies below the first excitation threshold of H. Similar work on 1P and 3P states has been performed also [66].

The use of Fock's coordinates to continuum states and doubly excited states suggests itself from the foregoing discussion. The great merit of Fock's coordinates is that they treat the two electrons in the $e - H$ or $e - He^+$ system on the same footing. Furthermore, the limit $R \rightarrow \infty$ includes alternative final-state possibilities: (a) $r_1 \rightarrow \infty$, $r_2 \rightarrow \text{finite}$, (b) $r_1 \rightarrow \text{finite}$, $r_2 \rightarrow \infty$, or (c) $r_1 \rightarrow \infty$, $r_2 \rightarrow \infty$. Case (a) or (b) corresponds to excitation and case (c) to ionization. Therefore, if one works out a reasonable theory in terms of Fock's coordinates, results should pertain to both excitation and ionization, and therefore to the competition between the two processes. From this point of view, it is not at all surprising [57] to see Wannier [67] and Rau [68] develop the theory of the threshold ionization by use of Fock's coordinates. Analyses of electron correlations in doubly excited states of H^- and He have recently been a subject of intense study [69-75]. When theory in this direction is fully developed, we shall have an adequate basis set with which a

wavefunction $\psi(\vec{r}_1, \dots, \vec{r}_N, \vec{r}_{N+1})$ for any e-A scattering state can be expanded more efficiently with full account of correlations between the incident electron and the excited atomic electron.

Finally, we must discuss a different line of development, i.e., the R-matrix theory [76-80]. This theory starts with the crucial recognition that the close-coupling expansion, Eq. (21), is suitable only for large r_{N+1} and that, once the incident electron approaches the close neighborhood of the atomic electrons, all the electrons should be treated similarly (in nearly the same way as a bound state). Therefore, it is logically suitable to separate the configuration space into two regions, i.e., an external region ($r_{N+1} > a$) and an internal region ($r_{N+1} < a$), a being a suitably chosen radius and to treat the two regions differently. Because the basic forces in atomic interactions are Coulombic and thus of long range, one may wonder if a reasonable choice of the boundary radius a is possible at all. Indeed, the R-matrix theory was first developed by Wigner and co-workers [81-83] with specific reference to nuclear reactions for which basic forces are short-ranged.

As long as we consider electron collisions with an atom initially in the ground state (or in a low-lying state), the atomic eigenfunction is exponentially declining at large distances. Therefore, if we take $a = 10 \sim 25 a_0$, practically all the ground-state charge distribution is enclosed in the sphere $r < a$, and atomic transitions always occur within it. Moreover, the exchange interactions between the incident electron and the atomic electrons, which give rise to complicated terms in the close-coupling equations, are non-vanishing only within the sphere.

In the internal region $r < a$, the total wavefunction is expressed as

$$\psi_k = \Omega \sum_{ij} c_{ijk} \Phi_i v_j + \sum_j d_{jk} \tilde{\Phi}_j, \quad (30)$$

where Φ_i (the channel functions) are products of an atomic eigenstate ϕ_i and the spin angular part of the incident electron wavefunction, and $\tilde{\Phi}_j$ are $(N+1)$ -electron bound-state wavefunctions that describe any resonance explicitly. The radial functions $v_j(r)$ are characteristic of the R-matrix theory, and form a basis set over $0 \leq r \leq a$ with the boundary condition

$$v_j(0) = 0, \quad (31)$$

$$\frac{a}{v_j(r)} \frac{dv_j(r)}{dr} \Big|_{r=a} = b_i \quad (32)$$

The discrete diagonalization of the Hamiltonian

$$(\psi_k, H\psi_k) = E_k \delta_{kk} \quad (33)$$

determines the expansion coefficients c_{ijk} and d_{jk} .

In the so-called eigenchannel method [79,80], E_k is preassigned to be the energy E of interest, and b_i come out as eigenvalues of the problem. Then ψ_k is nothing but the wavefunction ψ_E at energy E .

In the treatment by Burke and co-workers [76-78], b_i is fixed (usually at zero) and E_k are eigenvalues. Then ψ_E must be approximated as

$$\psi_E = \sum_k A_{Ek} \psi_k \quad (34)$$

The R matrix is defined as

$$R_{ij}(E) = \sum_k \frac{\gamma_{ki} \gamma_{kj}}{E_k - E} \quad (35)$$

where

$$\gamma_{ki} = \sum_j c_{ijk} v_j(a) \quad (36)$$

The R matrix connects the radial wavefunctions $v_i(a)$ at the surface to the external radial wavefunctions $u_j(r)$ as

$$v_i(a) = \sum_j R_{ij}(E) \left[a \frac{du_j}{dr} - b_j u_j \right]_{r=a} \quad (37)$$

In the external region $r > a$, one must solve a set of equations for u_j , which may be uncoupled or may be coupled only by multipole interactions expressed in terms of local potentials. However, it is necessary to obtain two independent solutions for each channel, say $s_j(r)$ and $c_j(r)$ which asymptotically behave as a sine and cosine function, respectively. An appropriate linear combination

$$u_j(r) = s_j(r) + \sum_i c_i(r) K_{ij} \quad (38)$$

then must be determined consistent with Eq. (37). The coefficients K_{ij} thus fixed form the K matrix, from which all cross sections are

derived according to standard formulas. The resulting K matrix should come out insensitive to the boundary radius a , if the method is to be successful.

Results of many calculations [78] show the great power of the R-matrix method, especially for excitations of atoms to lower excited states by slow electrons. Currently unsolved problems are ionization and transitions involving very high discrete states. The difficulty here is twofold: first, an appropriate a must be very large and therefore many R-matrix basis functions are needed for the internal region, and second, the connection of the solution with the external region is complicated for ionization where two electrons go out. Some merger of the R-matrix theory with the use of Fock's coordinates might be a suitable line of approach.

This observation leads to a personal outlook for future work. Suppose we attempt to solve the motion of two electrons in an internal region $R < a$ of the Fock space spanned by R, α, θ_{12} for S states (more generally, by a few more variables as well). Because the potential is a function of the three or more variables, the problem is, so to speak, isomorphic to the scattering of a single particle in a nonspherical potential, e.g., to the electron scattering in a static molecular field; indeed, the problem is even more similar to a chemical reaction $A + BC \rightarrow AB + C$ on a single adiabatic-potential surface. In all these examples, the potential is essentially of two, three, or higher dimension in such a way that it disallows any exact separation of variables in the Schrödinger equation. Consequently, progress in any one of those superficially unrelated fields can be a rich food for growth in another of those fields. In this respect, recent developments of scattering theory for nonspherical potentials, e.g., in Refs. 84 and 85, deserve full attention.

ACKNOWLEDGEMENTS

I want to thank Professor U. Fano for valuable discussions throughout the preparation of the present text, and also Dr. J. L. Dehmer and Dr. C. M. Lee for critical reading of an earlier manuscript.

REFERENCES

1. H. Bethe, Ann. Phys. (Leipzig) 5, 325 (1930).
2. H. Bethe, in Handbuch der Physik, Ed. H. Geiger and K. Scheel (Springer, Berlin, 1933), Vol. 24/1, p. 273.

3. M. Inokuti, *Rev. Mod. Phys.* 43, 297 (1971).
4. M. Inokuti, in Invited Papers and Progress Reports, VIIth International Conference on the Physics of Electronic and Atomic Collisions, Amsterdam, 1971, Ed. T. R. Govers and F. J. de Heer (North-Holland, Amsterdam, 1972) p. 327.
5. E. N. Lassette and A. Skerbele, in Methods of Experimental Physics, Vol. 3, Molecular Physics, Part B, Ed. D. Williams (Academic Press, New York, 1974), Chapter 7.2, p. 868.
6. Y.-K. Kim and M. Inokuti, *Phys. Rev.* 175, 176 (1968).
7. U. Amaldi, Jr. and C. C. degli Atti, *Nuovo Cim.* 66A, 129 (1970).
8. V. G. Levin, V. G. Neudatchin, A. V. Pavlitchenkov, and Yu. F. Smirnov, *J. Chem. Phys.* 63, 1541 (1975).
9. R. Camilloni, A. G. Guidoni, R. Tiribelli, and G. Stefani, *Phys. Rev. Letters* 29, 618 (1972).
10. A. G. Guidoni, G. Missoni, R. Camilloni, and G. Stefani, in Proceedings of the International Symposium on Electron and Photon Interactions with Atoms in Honor of Ugo Fano, Stirling, Scotland, 16-19 July 1974. (Plenum Press, New York, 1975) p.
11. E. Weigold, S. T. Hood, and I. E. McCarthy, *Phys. Rev. A* 11, 566 (1975).
12. A. Ugbabe, E. Weigold, and I. E. McCarthy, *Phys. Rev. A* 11, 576 (1975).
13. U. Fano, *Phys. Rev.* 95, 1198 (1954).
14. Y.-K. Kim and M. Inokuti, *Phys. Rev.* 184, 38 (1969).
15. K. L. Bell, D. J. Kennedy, and A. E. Kingston, *J. Phys. B* 1, 204 (1968).
16. K. L. Bell, D. J. Kennedy, and A. E. Kingston, *J. Phys. B* 2, 26 (1969).
17. J. van den Bos, *Physica* 42, 254 (1969).
18. R. Vanderpoorten, *Physica* 48, 254 (1970).
19. K. E. Banyard and G. J. Seddon, *J. Phys. B* 7, 429 (1974).
20. Y.-K. Kim and P. S. Bagus, *Phys. Rev. A* 8, 1739 (1973).
21. W. D. Robb, *J. Phys. B* 7, 1006 (1974).
22. K. E. Banyard and G. K. Taylor, *Phys. Rev. A* 10, 1019 (1974).
23. C. A. Wells and K. J. Miller, *Phys. Rev. A* 12, 17 (1975).
24. S. L. Davis and O. Sinanoğlu, *J. Chem. Phys.* 62, 3664 (1975).
25. J. P. Desclaux and Y.-K. Kim, *J. Phys. B* 8, 1177 (1975).
26. H. Ehrhardt, K. H. Hesselbacher, K. Jung, and K. Willmann, Case Studies in Atomic Collision Physics II. Ed. E. W. McDaniel and M. R. C. McDowell, North-Holland Publishing Co., Amsterdam-London, Chap. 3., p. 159 (1972).
27. M. J. van der Wiel, Lectures this Institute.

28. V. L. Jacobs, Phys. Rev. A 10, 499 (1974).
29. W. D. Robb, S. P. Rountree, and T. Burnett, Phys. Rev. A 11, 1193 (1975).
30. T. Brunett, S. P. Rountree, G. Doolen, and W. D. Robb, to appear in Phys. Rev. A (1975).
31. V. V. Balashov, S. S. Lipovetskii, and V. S. Senashenko, Zh. Eksp. Teor. Fiz. 63, 1622 (1972). [Engl. transl.: Soviet Phys. — JETP 36, 858 (1973).]
32. V. V. Balashov, S. S. Lipovetskii, and V. S. Senashenko, Opt. Spektrosk. 35, 11 (1973). [Engl. transl.: Opt. Spectrosc. 35, 6 (1973).]
33. M. J. van der Wiel, Phys. Letters 41A, 389 (1972).
34. M. Ya. Amus'ya, N. A. Cherepkov, and S. I. Sheftel', Zh. Eksp. Teor. Fiz. 58, 618 (1970) [Engl. transl.: Sov. Phys. — JETP 31, 332 (1970)].
35. M. Ya. Amusia, in Atomic Physics 2. Proceedings of the Second International Conference on Atomic Physics, Oxford, 1970, Ed. P. G. H. Sandars (Plenum Press, London, 1971), p. 249.
36. M. Ya. Amusia, S. I. Sheftel, N. A. Cherepkov, and L. V. Chernysheva, Phys. Letters 40A, 5 (1972).
37. M. Ya. Amusia, N. A. Cherepkov, R. K. Janev, S. I. Sheftel, and Dj. Živanović, J. Phys. B 6, 1028 (1973).
38. G. J. Schulz, Rev. Mod. Phys. 45, 378 (1973).
39. G. J. Schulz, Rev. Mod. Phys. 45, 423 (1973).
40. A. Kasdan and W. C. Lineberger, Phys. Rev. A 10, 1658 (1974).
41. D. L. Moores and D. W. Norcross, Phys. Rev. A 10, 1646 (1974).
42. C. M. Lee, Phys. Rev. A 11, 1692 (1975).
43. E. A. Hylleraas, Rev. Mod. Phys. 35, 421 (1963).
44. T. Kinoshita, Phys. Rev. 105, 1490 (1957).
45. C. L. Pekeris, Phys. Rev. 126, 1470 (1962).
46. Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A 4, 516 (1971).
47. K. Frankowski and C. L. Pekeris, Phys. Rev. 146, 46 (1966).
48. J. H. Bartlett, Jr., J. J. Gibbons, Jr., and C. G. Dunn, Phys. Rev. 47, 679 (1935).
49. V. A. Fock. Izv. Akad. Nauk S.S.S.R., Ser. Fiz. 18, 161 (1954) [Engl. transl.: Kgl. Norske Videnskab. Selskabs Forh. 31, 138 (1958)].
50. F. T. Smith, Phys. Rev. 120, 1058 (1960).
51. D. L. Knirk, Phys. Rev. Letters 32, 651 (1974).
52. A. M. Ermolaev and G. B. Sochilin, Dokl. Akad. Nauk S.S.S.R. 155, 1050 (1964) [Engl. transl.: Soviet Phys. — Doklady 9, 292 (1964)].

53. G. P. Burke and K. Smith, *Rev. Mod. Phys.* 34, 458 (1962).
54. K. Smith, The Calculation of Atomic Collision Processes (Wiley-Interscience, New York, 1971).
55. P. G. Burke and M. J. Seaton, in Methods in Computational Physics 10, 1 (1971).
56. P. G. Burke, *Comments Atom. Mol. Phys.* 3, 31 (1972).
57. U. Fano, *Comments Atom. Mol. Phys.* 1, 159 (1970).
58. H. Feshbach, *Ann. Phys. (N.Y.)* 19, 287 (1962).
59. R. J. Damburg and S. Geltman, *Phys. Rev. Letters* 20, 485 (1968).
60. S. Geltman and P. G. Burke, *J. Phys. B* 3, 1062 (1970).
61. A. J. Taylor and P. G. Burke, *Proc. Phys. Soc. (London)* 92, 336 (1967).
62. R. K. Nesbet, *Comput. Phys. Commun.* 6, 275 (1973).
63. R. S. Oberoi and R. K. Nesbet, *Phys. Rev. A* 8, 2696 (1973).
64. L. D. Thomas, R. S. Oberoi, and R. K. Nesbet, *Phys. Rev. A* 10, 1605 (1974).
65. C. Schwartz, *Phys. Rev.* 124, 1468 (1961).
66. R. L. Armstead, *Phys. Rev.* 171, 91 (1968).
67. G. H. Wannier, *Phys. Rev.* 90, 817 (1953).
68. A. R. P. Rau, *Phys. Rev. A* 4, 207 (1971).
69. J. H. Macek, *Phys. Rev.* 160, 170 (1967).
70. J. H. Macek, *J. Phys. B* 1, 831 (1968).
71. C. D. Lin, *Phys. Rev. A* 10, 1986 (1974).
72. U. Fano and C. D. Lin, in Invited Papers and Progress Reports, VIIIth International Conference on the Physics of Electronic and Atomic Collisions, Beograd, 1973. Ed. B. C. Cobić and M. V. Kurepa (Institute of Physics, Beograd, 1974), p. 229.
73. U. Fano and C. D. Lin, in Atomic Physics 4. Proceedings of the IVth International Conference on Atomic Physics, Heidelberg, 1974, Ed. G. zu Putlitz, E. W. Weber, and A. Winnacker (Plenum Press, New York, 1975), p. 47.
74. U. Fano, in Invited Papers and Progress Reports, IXth International Conference on the Physics of Electronic and Atomic Collisions, Seattle, 1975, Ed. J. S. Risley and R. Geballe (to be published by University of Washington Press, Seattle).
75. U. Fano, Lectures at this Institute.
76. P. G. Burke, A. Hibbert, and W. D. Robb, *J. Phys. B* 4, 153 (1971).
77. P. G. Burke, *Comments Atom. Mol. Phys.* 4, 157 (1973).
78. P. G. Burke and W. D. Robb, The R-matrix theory of atomic processes, to appear in *Advanced in Atomic and Molecular*

Physics (1975).

79. U. Fano and C. M. Lee, Phys. Rev. Letters 31, 1573 (1973).
80. C. D. Lin, Phys. Rev. A 10, 1986 (1974).
81. E. P. Wigner and L. Eisenbud, Phys. Rev. 72, 29 (1947).
82. A. M. Lane and R. G. Thomas, Rev. Mod. Phys. 30, 257 (1958).
83. G. Breit, in Handbuch der Physik, Ed. S. Flügge (Springer, Berlin, 1959), Vol. 41/1, p. 1.
84. Yu. M. Demkov and V. S. Rudakov, Zh. Eksp. Teor. Fiz. 59, 2035 (1970) [Engl. transl.: Sov. Phys.—JETP 32, 1103 (1971)].
85. D. Dill and J. L. Dehmer, J. Chem. Phys. 61, 692 (1974).